J. Am. Ceram. Soc., 93 [9] 2415–2418 (2010)
DOI: 10.1111/j.1551-2916.2010.03731.x
© 2010 The American Ceramic Society

journal

Rapid, Low-Temperature Synthesis of β-SiC Nanowires from Si and Graphite

Hui-Ling Zhu, Fu-Dong Han, Ning Lun, Yong-Xin Qi, Yu-Jun Bai,† Jian-Qiang Bi, Xiang-Lin Meng, Bo Zhang, Yun Wang, Jiu-Rong Liu, and Run-Hua Fan

Key Laboratory for Liquid-Solid Structural Evolution and Processing of Materials (Ministry of Education), Shandong University, Jinan 250061, China

β-SiC nanowires were synthesized at a temperature as low as 150°C by the reaction of Si and graphite induced by an additional reaction between Na and S. Characterization by X-ray diffraction, high-resolution transmission electron microscopy, IR spectra, and Raman spectra demonstrates the formation of curly β-SiC nanowires with several millimeters in length and 50–70 nm in diameter. Also, a prominent peak at 387 nm is observed in the visible photoluminescence emission. Besides the temperature, the molar ratio of S to Si (or graphite) has significant influence on the synthesis of SiC at relatively low temperatures.

I. Introduction

As a wide-band gap semiconductor material, SiC has attracted a great deal of scientific and commercial interest because of the countless applications resulting from its unique properties such as good mechanical behavior, outstanding thermal and chemical stability, large avalanche breakdown field, excellent thermal conductivity, high electron saturation velocity,[1] high stability in aggressive environment, and chemical inertness.[2] Particularly, SiC nanocrystals possess outstanding mechanical and field emission properties substantially exceeding those of the bulk.[3,4] So it is not surprising that uninterrupted progress has been made towards the synthesis of nanoscale SiC by various methods, such as decomposition of organic Si compounds,[5] high-temperature reaction of carbon nanotubes with SiO,[6,7] Si–I_2,[8] and Si–SiO_2 powder mixture,[9] reduction–carburization route using Si powders, CCl_4, and Na as reagents,[10] laser ablation,[11] arc-discharge process,[12] chemical vapor deposition (CVD),[13] and physical vapor deposition.[14]

A simple route to prepare SiC can be realized by the direct reaction of Si and graphite. Though the reaction between Si and graphite (Si+C = SiC) is thermodynamically spontaneous ($\Delta_r G_m^\theta = -62.8\,kJ/mol$) and exothermic ($\Delta_r H_m^\theta = -65.3\,kJ/mol$),[15] it is difficult to occur at low temperature due to the low thermodynamic values. Narayan *et al.*[16] fabricated β-SiC using pellets consisting of Si and carbon powders by combustion synthesis at 2000°C. Kholmanov *et al.*[17] synthesized SiC nanorods at a temperature of 1200°C from Si and amorphous carbon powders mixed by ball milling. Zhou *et al.*[18] prepared β-SiC from a solid carbon and Si source by hot filament CVD with a filament temperature of 2200°C. It is apparent that the methods mentioned above require either high temperature or long reaction time, and the product is also accompanied with some insoluble refractory metal carbides.[19] So, it is meaningful to explore other approaches to prepare SiC at low temperatures within short duration.

In this work, a new route was proposed to synthesize β-SiC nanocrystals at a temperature as low as 150°C by the reaction of Si and graphite, which was induced by the reaction of Na and S. This is an energy-saving, cost-effective approach to prepare SiC nanocrystals by the simple reaction between Si and graphite.

II. Experimental Procedure

(1) Synthesis of SiC

Analytically pure grade Si powder, graphite powder, Na, and S (all purchased from Tianjin Chemical Reagent Corp., Tianjin, China) were used as raw materials. A series of experiments were carried out with the same amount of Si (0.7 g or 0.025 mol) and graphite (0.3 g or 0.025 mol) to understand the influence of the additional reaction between Na and S on the synthesis of SiC, and to analyze the reaction mechanism. Table I listed the primary experiments designed, where the molar ratio of S to Si (or

Table I. Experiments Designed

Experiment number	Na (g)	S (g)	Molar ratio of S to Si	Temperature (°C)
1	4	2.4	3:1	150
2	4	2.4	3:1	300
3	3	1.6	2:1	300
4	2	0.8	1:1	300
5	2	0.8	1:1	600

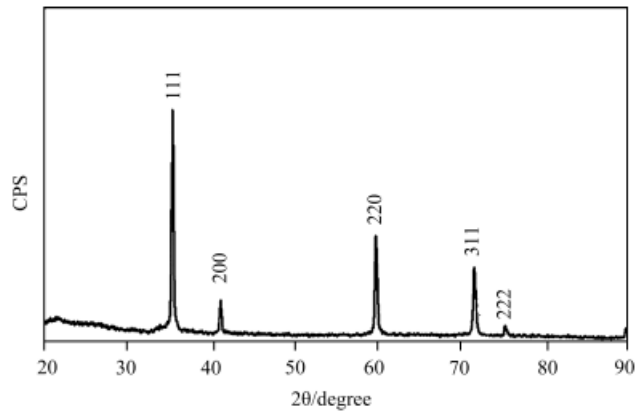

Fig. 1. X-ray powder diffraction patterns of the product obtained from Experiment 1.

N. Padture—contributing editor

Manuscript No. 27332. Received January 5, 2010; approved February 8, 2010.
This work was supported by the National Natural Science Foundation of China (No. 50972076, 50872072 and 50772061), Shandong Province Natural Science Foundation (Y2008F26 and Y2008F40), Science and Technology Development Project of Shandong Province (2009GG10003001, 2009GG10003003), and Special Fund for Postdoctoral Innovative Project of Shandong Province (200702024).
†Author to whom correspondence should be addressed. e-mail: byj97@126.com

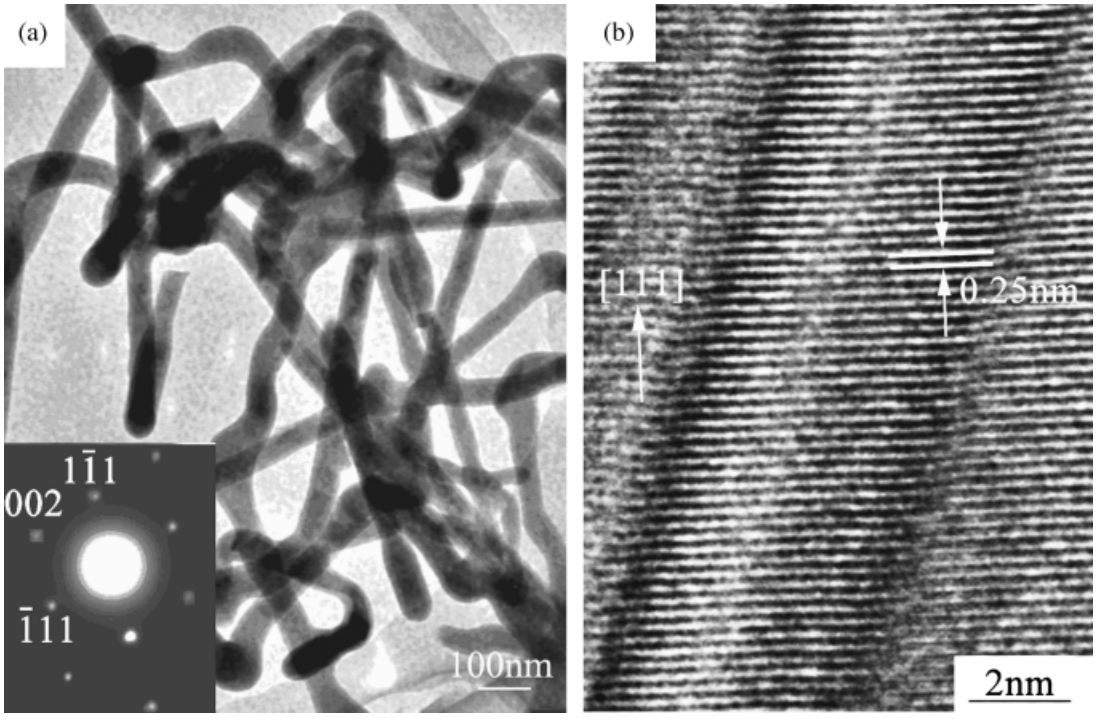

Fig. 2. High-resolution transmission electron microscope images and the corresponding selected area electron diffraction pattern (a) of the product obtained from Experiment 1, and the lattice fringe image of a single nanowire (b).

graphite) (MRSS) is 3:1, 2:1, and 1:1 with the designated reaction temperatures of 600°, 300°, and 150°C, with the same durations of 5 h.

In a typical procedure (Experiment 1), 0.7 g Si powder, 0.3 g graphite powder, 2.4 g (0.075 mol) S, and 4 g (0.174 mol) Na were mixed and put into a stainless-steel autoclave with a capacity of 30 mL, then the autoclave was sealed and heated in an electronic oven to 150°C for 5 h. When the autoclave was cooled to ambient temperature naturally, the product was collected and washed several times with anhydrous ethanol, concentrated sodium hydroxide solution, aqueous $HClO_4$, and deionized water successively to remove the residual Na, Si, graphite, and the Na_2S byproduct. The final product was dried at 50°C for 8 h and gray powder was ultimately obtained.

(2) Characterization of the Product

X-ray powder diffraction (XRD) patterns were obtained on a Dmax-rc diffractometer (Rigaku, Tokyo, Japan) with Ni-filtered Cu$K\alpha$ radiation ($V = 40$ kV, $I = 50$ mA) at a scanning rate of 4°/min. The morphology of SiC nanocrystals was examined using a Tecnai 20U-Twin high-resolution transmission electron microscope (HRTEM, Philips, Eindhoven, the Netherlands) with a point-to-point resolution of 0.19 nm operating at 200 kV. Fourier transform infrared measurement was conducted on a Bruker Vector 22 spectrometer (Bruker, Russ, Germany). Raman spectra were collected on a Renishaw confocal Raman microspectroscopy (Renishaw Co. Ltd., Gloucestershire, U.K.) with a laser excitation wavelength of 780 nm. The photoluminescence (PL) of the product was measured by a LabRAM HR800 confocal Laser MicroRaman Spectrometer (HORIBA Jobin Yvon Co. Ltd., Longjumeau, France) under an excitation wavelength of 325 nm.

III. Results and Discussion

Figure 1 shows the XRD patterns of the product obtained from Experiment 1. The diffraction peaks at $2\theta = 35.6°$, 41.4°, 60.0°,

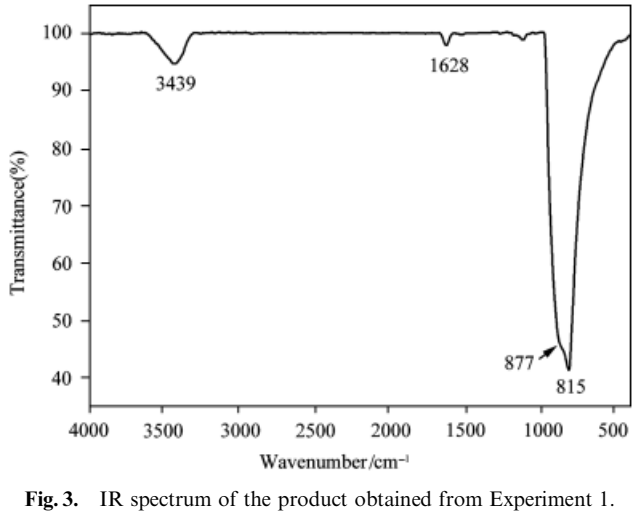

Fig. 3. IR spectrum of the product obtained from Experiment 1.

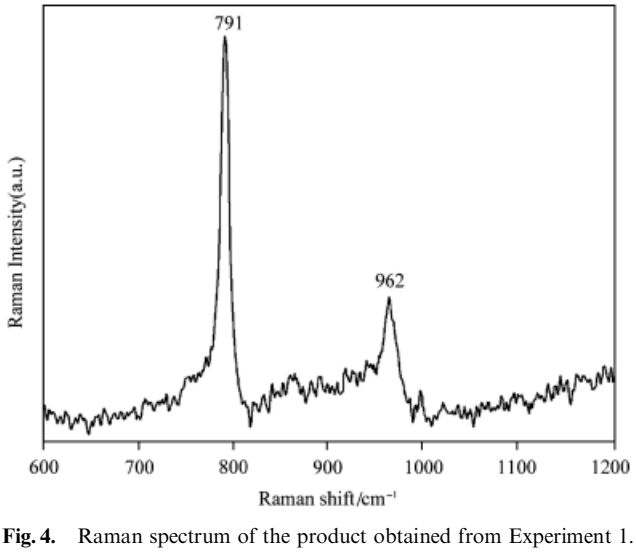

Fig. 4. Raman spectrum of the product obtained from Experiment 1.

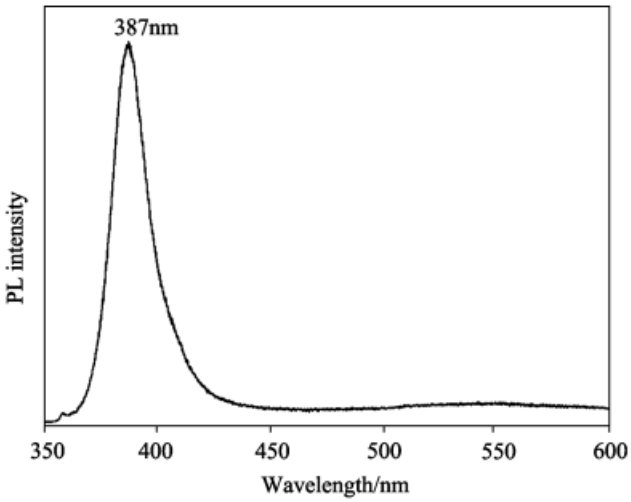

Fig. 5. Room-temperature photoluminescence spectrum of the product obtained from Experiment 1. PL, photoluminescence.

71.7°, and 75.5° can be respectively ascribed to the (111), (200), (220), (311), and (222) planes of β-SiC with a calculated lattice constant $a = 4.363$ Å, which are in good agreement with those in JCPDS 29-1129, clearly indicating the occurrence of the reaction between Si and graphite. With the MRSSs of 2:1 and 3:1, the lowest temperatures to obtain well-crystallized β-SiC are 300° and 150°C, respectively. However, when the temperature is below 150°C with the MRSS <3:1 or 600°C with the MRSS <1:1, no SiC can be identified in the product.

Figure 2 shows the HRTEM image of the product obtained from Experiment 1. From Fig. 2(a), the product is comprised primarily of flexural nanowires with 50–70 nm in diameter and several micrometers in length. The corresponding selected area electron diffraction pattern in Fig. 2(a) demonstrates that the nanowires are single crystalline β-SiC. Figure 2(b) is the lattice fringe image of a single nanowire in Fig. 2(a), the regularly arranged lattice fringe reveals the high crystallinity of the nanowire. The interplanar spacing of 0.25 nm agrees well with that between two adjacent (111) planes of β-SiC, indicating that the nanowire grows along the [111] direction.

Figure 3 displays the IR spectrum of the product obtained from Experiment 1. The pronounced absorption peaks around 815 and 877 cm^{-1} are associated with the transverse optical (TO) vibration mode[20] and the stretching mode of Si–C bond, respectively. The absorption bands centered at 3439 and 1628 cm^{-1} can be attributed to the stretching and bending vibration of H–O–H owing to the water absorbed on the surface.

Figure 4 is the Raman spectrum of the product obtained from Experiment 1. The bands around 791 and 962 cm^{-1} correspond to the TO and longitudinal optical (LO) phonon at the Γ point of β-SiC, respectively. Compared with the values of the bulk SiC,[21] the significant red shifts of 5 and 10 cm^{-1} for the TO and LO modes are due to the size confinement effect,[22] residual stress,[23] and surface disorder.[24] Considering the XRD patterns and IR spectra, all the products obtained at temperatures above 150°C with MRSSs >3:1 or at the temperatures above 300°C with MRSSs >2:1 are comprised of nanocrystalline β-SiC.

Figure 5 shows a room-temperature PL spectrum of the SiC nanowires under a 325 nm excitation. The curving nanowires show an emission band around 387 nm, corresponding to a band gap energy of 3.22 eV, which is far higher than that of the bulk β-SiC (2.30 eV). The sharp emission band confirms the uniform size of the as-synthesized nanowires. Compared with the luminescence from the straight SiC nanowires[10] and films,[25] the emission from the curving SiC nanowires is obviously blue shifted. The shift may be ascribed to the flexural shape and size-confinement effect of the nanowires. The intrinsical reasons for the luminescence mechanism of curving SiC nanowires are presently unknown, and an in-depth study is underway.

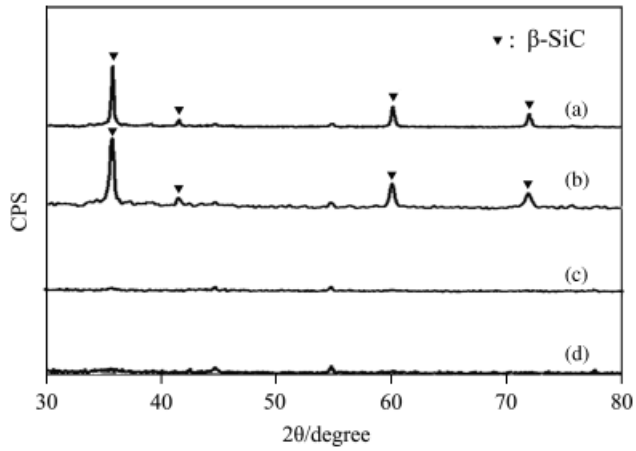

Fig. 6. X-ray powder diffraction patterns of the products obtained from Experiments 2 (a), 3 (b), 4 (c), and 5 (d).

In order to probe into the reaction mechanism, a series of experiments were carried out at various MRSSs and temperatures, as shown in Table I. No reaction occurs at 600°C between Si and graphite without the addition of Na and S. So the reaction between Na and S plays a crucial role in synthesizing SiC at low temperatures. Experiments 2, 3, 4, and 5 were designed to compare the effect of different MRSSs on the synthesis of SiC.

Figure 6 shows the XRD patterns of the products obtained from Experiments 2, 3, 4, and 5. No crystalline SiC can be detected in the products obtained at the MRSS of 1:1 even at a reaction temperature of 600°C. At the MRSS of 3:1, SiC with high crystallinity can be prepared at a temperature as low as 150°C. By and large, once the reaction occurs, the products are hardly affected by the reaction temperature and holding time.

According to the careful observations on the products and the above analysis, a brief reaction mechanism can be proposed as follows. It is too difficult for the direct reaction between Si and graphite to occur at low temperature due to the low thermodynamic values. Whereas the reaction between Na and S ($2Na+S = Na_2S$) may happen at low temperature with an instantaneous and high heat release ($\Delta_r G_m^\theta = -349.8\,kJ/mol$, $\Delta_r H_m^\theta = -364.8\,kJ/mol$).[15] If the heat released by the reaction of Na and S is large enough, the reaction between Si and graphite could be induced to form SiC. Meanwhile, when the temperature is above 150°C, Na and S are in liquid or sublimed state, providing a sort of mass transfer between Si and graphite and favoring to the formation of SiC nanowires. However, other intermediates, such as SiS_2 which may form above 600°C,[26] could also generate during the reaction. The intermediates can be reduced by the excess Na to produce Si, and the renascent element may further combine with graphite into SiC. So the overall reaction between the reactants can be expressed by Eq. (1), where n is the MRSS.

$$Si + C + 2nNa + nS \rightarrow SiC + nNa_2S \quad (1)$$

Associated with the independence of holding time on the synthesis of SiC, it is reasonably believed that the reaction is very fast once happens. The low reaction temperature and the quite short reaction time are both responsible for the formation of nanoscale β-SiC with uniform size.

IV. Conclusions

Induced by the additional reaction between Na and S, nanocrystalline β-SiC have been efficiently synthesized via the direct reaction between Si and graphite at a considerably low temperature of 150°C. The product consists dominantly of curving SiC nanowires with several millimeters in length and 50–70 nm in diameter. This approach has inherent advantages in synthesizing

nanocrystalline β-SiC, including a simple production procedure, the low-cost raw materials, the low reaction temperature and short duration, and the high yield, and can be easily scaled up. A similar approach can also be extended to prepare other refractory nanomaterials, which is our recent research focus in progress.

References

[1]H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, "Large-Band-Gap SiC, III–V Nitride, and II–VI ZnSe-Based Semiconductor Device Technologies," *J. Appl. Phys.*, **76** [3] 1363–98 (1994).

[2]G. Pensl, H. Morkoc, B. Monemar, and E. Janzen, *Silicon Carbide, III-Ni-Trides, and Related Materials*, pp. 264–8, 2678–82. Uetikon/Trans. Tech., Zurich/Switzerland, 1998.

[3]X. F. Zhang, M. E. Sixta, and L. C. De Jonghe, "Grain Boundary Evolution in Hot-Pressed ABC–SiC," *J. Am. Ceram. Soc.*, **83** [11] 2813–20 (2000).

[4]E. W. Wong, P. E. Sheehan, and C. M. Lieber, "Nanobeam Mechanics: Elasticity, Strength, and Toughness of Nanorods and Nanotubes," *Science*, **277** [5334] 1971–5 (1997).

[5]A. Addamiano, "Preparation and Properties of 2H SiC Crystals," *J. Cryst. Growth*, **58** [3] 617–22 (1982).

[6]D. Zhou and S. Seraphin, "Production of Silicon Carbide Whiskers from Carbon Nanoclusters," *Chem. Phys. Lett.*, **222** [3] 233–8 (1994).

[7]Z. W. Pan, H. L. Lai, F. C. K. Au, X. Duan, W. Y. Zhou, W. S. Shi, N. Wang, C. S. Lee, N. B. Wong, S. T. Lee, and S. S. Xie, "Oriented Silicon Carbide Nanowires: Synthesis and Field Emission Properties," *Adv. Mater.*, **12** [16] 1186–90 (2000).

[8]H. J. Dai, E. W. Wong, Y. Z. Lu, S. S. Fan, and C. M. Lieber, "Synthesis and Characterization of Carbide Nanorods," *Nature*, **375** [6534] 769–72 (1995).

[9]W. Q. Han, S. S. Fan, Q. Q. Li, W. J. Liang, B. L. Gu, and D. P. Yu, "Continuous Synthesis and Characterization of Silicon Carbide Nanorods," *Chem. Phys. Lett.*, **265** [3–5] 374–8 (1997).

[10]J. Q. Hu, Q. Y. Lu, K. B. Tang, B. Deng, R. R. Jiang, Y. T. Qian, W. C. Yu, G. E. Zhou, X. M. Liu, and J. X. Wu, "Synthesis and Characterization of SiC Nanowires Through a Reduction Carburization Route," *J. Phys. Chem. B*, **104** [22] 5251–4 (2000).

[11]W. S. Shi, Y. F. Zheng, H. Y. Peng, N. Wang, C. S. Lee, and S. T. Lee, "Laser Ablation Synthesis and Optical Characterization of Silicon Carbide Nanowires," *J. Am. Ceram. Soc.*, **83** [12] 3228–30 (2000).

[12]T. Seeger, P. Kohler-Redlich, and M. Rühle, "Synthesis of Nanometer-Sized SiC Whiskers in the Arc-Discharge," *Adv. Mater.*, **12** [4] 279–82 (2000).

[13]Y. Kamlag, A. Goossens, I. Colbeck, and J. Schoonman, "Laser CVD of Cubic SiC Nanocrystals," *Appl. Surf. Sci.*, **184**, 118–22 (2001).

[14]J. W. Liu, D. Y. Zhong, F. Q. Xie, M. Sun, E. G. Wang, and W. X. Liu, "Synthesis of SiC Nanofibers by Annealing Carbon Nanotubes Covered with Si," *Chem. Phys. Lett.*, **348** [5–6] 357–60 (2001).

[15]J. A. Dean, *Lange's Handbook of Chemistry*, 15th edition, McGraw-Hill, New York, 1999.

[16]J. Narayan, R. Raghunathan, R. Chowdhury, and K. Jagannadham, "Mechanism of Combustion Synthesis of Silicon Carbide," *J. Appl. Phys.*, **75** [11] 7252–7 (1994).

[17]I. N. Kholmanov, A. Kharlamov, E. Barborini, C. Lenardi, A. Li Bassi, C. E. Bottani, C. Ducati, S. Maf, N. V. Kirillova, and P. Milani, "A Simple Method for the Synthesis of Silicon Carbide Nanorods," *J. Nanosci. Nanotech.*, **2** [5] 1–4 (2002).

[18]X. T. Zhou, N. Wang, H. L. Lai, H. Y. Peng, I. Bello, N. B. Wong, C. S. Lee, and S. T. Lee, "β-SiC Nanorods Synthesized by Hot lament Chemical Vapor Deposition," *Appl. Phys. Lett.*, **74** [26] 3942–4 (1999).

[19]P. Matteazzi and G. L. Caer, "Room-Temperature Mechanosynthesis of Carbides by Grinding of Elemental Powders," *J. Am. Ceram. Soc.*, **74** [6] 1382–90 (1991).

[20]H. Hobert, H. H. Dunken, G. Peiter, W. Stier, M. Diegel, and H. Stafast, "Vibrational Spectroscopy of SiC Thin Films Deposited by Excimer Laser Ablation," *Appl. Phys. A*, **69** [1] 69–76 (1999).

[21]Z. C. Feng, A. Mascarenhas, W. J. Choyke, and J. A. Powell, "Raman Scattering Studies for Chemical Vapor Deposited 3C–SiC Films on (100) Si," *J. Appl. Phys.*, **64** [6] 3176–86 (1988).

[22]S. L. Zhang, B. F. Zhu, F. M. Huang, Y. Yan, E. Y. Shang, S. S. Fan, W. G. Han, L. D. Zhang, and G. W. Men, "Effect of Disorders on Optical Phonon Raman Spectra in SiC Nanorods," *Solid State Commun.*, **111** [11] 647–51 (1999).

[23]Y. M. Lu and I. C. Leu, "Qualitative Study of Beta Silicon Carbide Residual Stress by Raman Spectroscopy," *Thin Solid Film*, **377–378** [1–2] 389–93 (2000).

[24]H. Hobert, H. H. Dunken, S. Urban, F. Falk, and H. Stafast, "Laser-Induced Change of Silicon Carbon Films Studied by Vibrational Spectroscopy," *Vib. Spectrosc.*, **29** [1–2] 177–82 (2002).

[25]H. W. Shim, K. C. Kim, Y. H. Seo, K. S. Nahm, E. K. Suh, H. J. Lee, and Y. G. Hwang, "Anomalous Photoluminescence from 3C–SiC Grown on Si(111) by Rapid Thermal Chemical Vapor Deposition," *Appl. Phys. Lett.*, **70** [13] 1757–9 (1997).

[26]S. Z. Yao, Y. B. Zhu, S. E. He, and L. H. Nie, "*Handbook of Chemical Reactions of Elements*". Education Press of Hunan, Changsha, 1998, 336pp. □